

There appears to be a direct correlation between the activation energies for the exchange of non-equivalent trifluoromethyl groups and the deviations from planarity of the HFAA ligands, but no correlation with the deviation of the U atom from the equatorial plane. On this basis ligand rotation has been proposed as the mechanism for the intramolecular exchange reaction in these compounds (Glavincevski & Brownstein, 1982).

References

DiSIPIO, L., TONDELLO, E., PELIZZI, G., INGLETTO, G. & MONTENERO, A. (1974). *Cryst. Struct. Commun.* **3**, 731–734.
GLAVINCEVSKI, B. & BROWNSTEIN, S. (1982). *Inorg. Chem.* In the press.

GRANT, D. F. & GABE, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.
HARGREAVES, A. (1955). *Acta Cryst.* **8**, 12–14.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
KRAMER, G. M., DINES, M. B., HALL, R. B., KALDOR, A., JACOBSON, A. J. & SCANLON, J. C. (1980). *Inorg. Chem.* **19**, 1340–1347.
LARSON, A. C. & GABE, E. J. (1978). *Computing in Crystallography*, edited by H. SCHENK, R. OLTJOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, p. 81. Delft Univ. Press.
LE PAGE, Y., GABE, E. J. & CALVERT, L. D. (1979). *J. Appl. Cryst.* **12**, 25–26.
LEVY, J. H. & WAUGH, A. B. (1977a). *J. Chem. Soc. Dalton Trans.* pp. 1628–1629.
LEVY, J. H. & WAUGH, A. B. (1977b). *J. Chem. Soc. Dalton Trans.* pp. 1630–1636.
LEVY, J. H. & WAUGH, A. B. (1977c). *J. Chem. Soc. Dalton Trans.* pp. 1636–1640.

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Structure of 1,2-Ethanedithiolatobis(triphenylphosphine)platinum(II), C₃₈H₃₄P₂PtS₂

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Abstract. $M_r = 811.86$, triclinic, $P\bar{1}$, $a = 19.086$ (9), $b = 9.876$ (3), $c = 9.706$ (4) Å, $\alpha = 77.69$ (3), $\beta = 80.85$ (3), $\gamma = 67.98$ (3)°, $Z = 2$, $V = 1651$ (2) Å³, $D_m = 1.7$ (1), $D_x = 1.633$ (1) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 4.714$ mm⁻¹, $T = 295$ K. Final $R = 0.048$ for 3160 observed reflections. The distances Pt–S(1) and Pt–S(2) are 2.328 (4) and 2.313 (4) Å, and Pt–P(1) and Pt–P(2) are 2.296 (3) and 2.281 (4) Å. The distances S(1)–C(1), S(2)–C(2) and C(1)–C(2) are 1.82 (2), 1.83 (1) and 1.45 (2) Å, respectively.

Introduction. Organosulfur derivatives of the transition metals are of significant interest due to the novel structures and properties of the complexes formed. Metal thiolates represent the most common type of this class of compound, platinum thiolates having been reported as early as last century (Hofmann & Rabe, 1897). More recent research has focused on controlling substitution–polymerization reactions to synthesize monomeric thiolate complexes (Hayter & Humiec, 1964; Rauchfuss & Roundhill, 1975; Rauchfuss, Shu & Roundhill, 1976). Of current interest to us are the monomeric complexes of the type Pt(SR)₂L₂. It has been suggested that the *cis* isomers are uncommon and that the monomeric thiolate complexes are unstable to polymerization (Lai & Shaver, 1981).

Recently the complexes *cis*-Pt(SH)₂(PPh₃)₂ (Schmidt & Hoffman, 1980) and Pt(SCH₂CH₂S)(PPh₃)₂ (Rauchfuss & Roundhill, 1975) have been prepared and *cis*-Pt(SH)₂(PPh₃)₂ characterized by single-crystal X-ray analysis (Briant, Hughes, Minshall & Mingos, 1980). The structure of Pt(SCH₂CH₂S)(PPh₃)₂ has been solved to determine that the compound is monomeric and to elucidate the coordination geometry about platinum.

Experimental. Yellow crystals from a chloroform–diethyl ether solution, D_m measured by flotation in 1,1,2,2-tetrachloroethane/1,2-dibromoethane, 0.062 × 0.141 × 0.183 mm, {100}, { $\bar{1}00$ }, {010} and {0 $\bar{1}0$ } faces developed, mounted on a glass fiber with c and spindle axes collinear; crystal belonged to a triclinic space group because no symmetry or systematic absences on oscillation or on zero, first, or second-level Weissenberg photographs, data collected for that crystal class, final lattice constants from least-squares refinement of reciprocal-lattice coordinates of 12 accurately centered reflections; automated Picker full-circle diffractometer, Zr filter, θ – 2θ step scan of 2.4° in 2θ , 20 steps deg⁻¹, 2.0 s step⁻¹, background of 20s before and after each scan, $\sigma^2(I_o) = \sigma_{\text{stat}}^2 + C^2 I_o^2$, $\sigma^2(I_o)$ the estimated variance in intensity, $C = 0.03$, I_o the intensity of the reflection, σ_{stat} the error from the

counting statistics, 2θ range 4 to 43° , 3778 unique reflections collected, 3160 observed [$I > 3\sigma(I)$]; three standard reflections monitored every 41 reflections showed no systematic deviations during collection, data corrected for Lorentz-polarization and absorption from optically measured crystal dimensions; transmission factors range from 0.51 to 0.76; Pt, S and P atomic positions from *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and Patterson maps, atomic positions found from Fourier mapping techniques; for 2896 reflections with $I \geq 5\sigma(I)$, $R_w = 0.080$ with non-H atoms refined isotropically; the Pt, S, and P atoms refining anisotropically gave $R = 0.044$ and $R_w = 0.054$; calculated H-atom positions checked on Fourier difference maps, assigned thermal parameters 1 \AA^2 greater than their bonded C atom; $R = 0.041$ and $R_w = 0.052$ with Pt, S, P, C(1), C(2) anisotropic, phenyl C atoms isotropic, H-atoms fixed; final refinement on F using 3160 reflections, $I \geq 3\sigma$, $R = 0.048$, $R_w = 0.057$; no adjustment for secondary extinction, parameter shifts on last cycle less than 1% of estimated error, goodness-of-fit 0.9493 with $w = 1/\sigma^2(F)$, atomic scattering factors from *International Tables for X-ray Crystallography* (1962), $F(000) = 803.9$, computer programs used from local library including modified versions of *ORFLS* (Busing, Martin & Levy, 1962), *ORFFE* (Busing, Martin & Levy, 1964), *ORTEP* (Johnson, 1965), *ORABS* (Wehe, Busing & Levy, 1962) and *MULTAN* (Main *et al.*, 1980).

Discussion. The asymmetric unit of the unit cell is shown in Fig. 1 with all atoms labelled. Final atomic parameters are given in Table 1 and interatomic distances and angles given in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and bond distances and angles in the phenyl rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38185 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

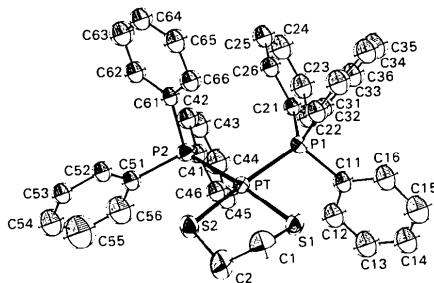


Fig. 1. *ORTEP* drawing of $\text{Pt}(\text{SCH}_2\text{CH}_2\text{S})(\text{PPh}_3)_2$ with 50% probability thermal ellipsoids showing the conformation of the thiaplatinacycle.

Table 1. Final positional parameters and isotropic temperature factors (\AA^2)

	x	y	z	U_{eq}^*/U_{iso}
Pt	0.23894 (3)	0.89387 (5)	0.36260 (5)	0.0313
S(1)	0.1445 (2)	0.8634 (4)	0.5367 (4)	0.050
S(2)	0.3063 (2)	0.6438 (4)	0.4249 (4)	0.047
P(1)	0.1570 (2)	1.1337 (3)	0.3117 (3)	0.036
P(2)	0.3399 (2)	0.9107 (4)	0.2083 (3)	0.038
C(1)	0.166 (1)	0.665 (2)	0.555 (2)	0.08
C(2)	0.246 (1)	0.580 (2)	0.570 (2)	0.07
C(11)	0.118 (1)	0.208 (1)	0.475 (1)	0.040 (3)
C(12)	0.166 (1)	0.200 (2)	0.569 (2)	0.059 (4)
C(13)	0.140 (1)	0.258 (2)	0.694 (2)	0.070 (5)
C(14)	0.065 (1)	0.312 (2)	0.728 (2)	0.069 (4)
C(15)	0.015 (1)	0.320 (2)	0.643 (2)	0.081 (5)
C(16)	0.040 (1)	0.268 (2)	0.508 (2)	0.062 (4)
C(21)	0.189 (1)	0.279 (1)	0.198 (1)	0.032 (3)
C(22)	0.200 (1)	0.390 (2)	0.249 (2)	0.052 (4)
C(23)	0.223 (1)	0.498 (2)	0.159 (2)	0.058 (4)
C(24)	0.235 (1)	0.495 (2)	0.018 (2)	0.060 (4)
C(25)	0.225 (1)	0.385 (1)	0.959 (1)	0.047 (3)
C(26)	0.201 (1)	0.279 (1)	0.054 (1)	0.041 (3)
C(31)	0.075 (1)	0.155 (1)	0.224 (1)	0.033 (3)
C(32)	0.055 (1)	0.039 (2)	0.222 (1)	0.049 (4)
C(33)	0.989 (1)	0.057 (2)	0.156 (2)	0.059 (4)
C(34)	0.946 (1)	0.197 (1)	0.096 (2)	0.061 (4)
C(35)	0.964 (1)	0.316 (2)	0.096 (2)	0.064 (4)
C(36)	0.032 (1)	0.294 (2)	0.162 (2)	0.054 (4)
C(41)	0.366 (1)	0.062 (1)	0.233 (1)	0.034 (3)
C(42)	0.390 (1)	0.158 (1)	0.122 (1)	0.042 (3)
C(43)	0.410 (1)	0.269 (1)	0.160 (2)	0.057 (4)
C(44)	0.407 (1)	0.284 (1)	0.291 (1)	0.062 (4)
C(45)	0.386 (1)	0.186 (1)	0.404 (2)	0.054 (4)
C(46)	0.364 (1)	0.081 (1)	0.370 (1)	0.043 (3)
C(51)	0.431 (1)	0.753 (1)	0.230 (1)	0.036 (3)
C(52)	0.447 (1)	0.634 (1)	0.167 (1)	0.040 (3)
C(53)	0.514 (1)	0.513 (1)	0.186 (1)	0.045 (3)
C(54)	0.564 (1)	0.511 (2)	0.265 (2)	0.073 (5)
C(55)	0.551 (1)	0.632 (3)	0.332 (2)	0.105 (7)
C(56)	0.483 (1)	0.753 (2)	0.311 (2)	0.081 (5)
C(61)	0.327 (1)	0.919 (1)	0.022 (1)	0.032 (3)
C(62)	0.385 (1)	0.924 (1)	0.914 (1)	0.044 (3)
C(63)	0.376 (1)	0.911 (2)	0.780 (2)	0.058 (4)
C(64)	0.315 (1)	0.895 (1)	0.752 (1)	0.050 (4)
C(65)	0.257 (1)	0.893 (2)	0.855 (2)	0.054 (4)
C(66)	0.263 (1)	0.904 (1)	0.994 (1)	0.041 (3)

* All Pt, P, S atoms and C(1) and C(2) have been refined anisotropically; all other C atoms have been refined isotropically. Calculated for non-H atoms from anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \dots + \beta_{12}hk + \dots)]$ as $U_{eq} = (a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33})/6\pi^2$.

Table 2. Interatomic distances (\AA) and angles ($^\circ$) excluding phenyl rings

Pt-S(1)	2.328 (4)	P(1)-C(21)	1.85 (1)
Pt-S(2)	2.313 (4)	P(1)-C(31)	1.83 (1)
Pt-P(1)	2.296 (3)	P(2)-C(41)	1.82 (1)
Pt-P(2)	2.281 (4)	P(2)-C(51)	1.85 (1)
S(1)-C(1)	1.82 (2)	P(2)-C(61)	1.84 (1)
S(2)-C(2)	1.83 (1)	C(1)-C(2)	1.45 (2)
P(1)-C(11)	1.82 (1)		
S(1)-Pt-S(2)	87.7 (1)	Pt-P(2)-C(41)	110.5 (4)
S(1)-Pt-P(1)	85.1 (1)	Pt-P(2)-C(51)	116.9 (4)
S(1)-Pt-P(2)	174.3 (1)	Pt-P(2)-C(61)	114.0 (4)
S(2)-Pt-P(1)	171.9 (1)	S(1)-C(1)-C(2)	112 (1)
S(2)-Pt-P(2)	88.4 (1)	S(2)-C(2)-C(1)	112 (1)
P(1)-Pt-P(2)	99.0 (1)	C(11)-P(1)-C(21)	103.5 (5)
Pt-S(1)-C(1)	100.4 (5)	C(11)-P(1)-C(31)	105.1 (6)
Pt-S(2)-C(2)	104.2 (5)	C(21)-P(1)-C(31)	100.7 (5)
Pt-P(1)-C(11)	109.9 (4)	C(41)-P(2)-C(51)	101.0 (5)
Pt-P(1)-C(21)	121.6 (4)	C(41)-P(2)-C(61)	112.6 (5)
Pt-P(1)-C(31)	114.5 (4)	C(51)-P(2)-C(61)	101.0 (5)

The crystal structure of $\text{Pt}(\text{SCH}_2\text{CH}_2\text{S})(\text{PPh}_3)_2$ shows an isolated monomeric unit having no Pt-Pt distance closer than 8.6 \AA and no intermolecular Pt-S

distance closer than 6.7 Å. The coordination geometry about Pt is planar but distorted from square planarity. The Pt, S(1), S(2), P(1) and P(2) atoms all lie within 0.092 (4) Å of the best least-squares plane through those atoms. The respective bond angles S(1)—Pt—S(2), P(1)—Pt—P(2), S(1)—Pt—P(1) and S(2)—Pt—P(2) are 87.7 (1), 99.0 (1), 85.1 (1) and 88.4 (1)°. The S(1)—Pt—S(2) bond angle of 87.7 (1)° is significantly larger than the S—Pt—S angle of 83.14 (8)° in the compound *cis*-Pt(SH)₂(PPh₃)₂. The difference is likely due to the conformational requirements of the thia-platinacycle. This thia-platinacycle is a five-membered ring with the C atoms in a staggered conformation. The angles about the two ring C atoms, S(1)—C(1)—C(2) and S(2)—C(2)—C(1), are both 112 (1)° as expected for saturated hydrocarbons. The C(1)—C(2) bond distance of 1.45 (2) Å is considerably shorter than the usual value of 1.54 Å for such bonds. Thermal motion may be contributing to this apparent shortening.

The deviation of the P(1)—Pt—P(2) bond angle of Pt(SCH₂CH₂S)(PPh₃)₂ from 90° can be accounted for by steric interactions of the triphenylphosphine groups. The P(1)—Pt—P(2) angle of 99.0 (1)° is larger than 97.65 (7)° found in *cis*-Pt(SH)₂(PPh₃)₂. The bond-angle difference between S(1)—Pt—P(1) of 85.1 (1)°, and S(2)—Pt—P(2) of 88.4 (1)° is unanticipated, but all non-bonded intermolecular S...phenyl hydrogen interactions are too long to cause any such distortions. The structure can therefore be described as a planar, monomeric, slightly distorted thiametallacycle with a puckered ring.

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References

- BRIANT, C. E., HUGHES, G. R., MINSHALL, P. C. & MINGOS, D. M. P. (1980). *J. Organomet. Chem.* **202**, C18—C20.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL—TM—305. Oak Ridge National Laboratory, Tennessee.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL—TM—306. Oak Ridge National Laboratory, Tennessee.
 HAYTER, R. G. & HUMIEC, F. S. (1964). *J. Inorg. Nucl. Chem.* **26**, 807—810.
 HOFMANN, K. A. & RABE, W. O. (1897). *Z. Anorg. Allg. Chem.* **14**, 293—296.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL—3794. Oak Ridge National Laboratory, Tennessee.
 LAI, R. D. & SHAVER, A. (1981). *Inorg. Chem.* **20**, 477—480.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1980). *MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 RAUCHFUSS, T. B. & ROUNDHILL, D. M. (1975). *J. Am. Chem. Soc.* **97**, 3386—3392.
 RAUCHFUSS, T. B., SHU, J. S. & ROUNDHILL, D. M. (1976). *Inorg. Chem.* **15**, 2096—2101.
 SCHMIDT, V. M. & HOFFMAN, G. G. (1980). *Z. Anorg. Allg. Chem.* **464**, 209—216.
 WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS*. Report ORNL—TM—229. Oak Ridge National Laboratory, Tennessee.

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Structure of *trans*-Dichlorobis(1-methylimidazole)palladium(II), [Pd(C₄H₆N₂)₂Cl₂]

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Abstract. $M_r = 341.52$, monoclinic, $P2_1/c$, $a = 5.1278$ (1), $b = 11.636$ (1), $c = 10.168$ (1) Å, $\beta = 97.402$ (4)°, $V = 601.64$ (4) Å³, $\lambda(\text{Ag } K\alpha) = 0.5608$ Å, $Z = 2$, $D_x = 1.885$ Mg m⁻³, $\mu(\text{Ag } K\alpha) = 9.85$ cm⁻¹, $F(000) = 306$, $T = 298$ K. Final $R = 0.040$ for 2162 reflections. The Pd atom lies on a symmetry centre, all other atoms are in general positions.

Introduction. The study of imidazole complexes with transition-metal ions is of interest as the ligand is closely related to biological systems involving the histidine residue.

On the other hand, although coordination compounds of Pt^{II} and Pd^{II} have been known for more than a century (Kauffman, 1976), the coordination chemis-